



INVESTIGATOR'S ANNUAL REPORT

National Park Service

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Reporting Year 2000	Park Yellowstone				
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Project Title (maximum 300 characters) Effects of Snowmobile Use on Semi-Volatile Organic Compounds in the Yellowstone National Park Snowpack					
Park-assigned Study #		Park-assigned Permit #		Permit Start Date	Permit Expiration Date
Study Starting Date Jan 15, 1999			Estimated Study Ending Date April 30, 2001		
Study Status (circle one): Completed <u>Continuing</u> X Suspended Terminated before completed					
Activity Type (circle one): <u>Research</u> Inventory Monitoring Education Other					
Subject/Discipline (circle one):	Ecology	Geo. Info. System (GIS)	Ichthyology	Recreation/ Aesthetics	Volcanology/
	Entomology	Geochemistry	Integrated Pest Mgmt.	Restoration – Cultural	Geothermal
	Environmental	Geohydrology	Invertebrates	Restoration – Natural	Water Quality
Agriculture	Monitoring	Geology – Coastal	Limnology	Sedimentol./ Stratigraphy	<u>Water Quantity</u>
<u>Air Quality</u>	Erosion/ Sedimentation	Geology – Fluvial	Mammalogy	Social Science – Economics	Water Rights
Anthropol./Ethnograph	Exotic Sp. – Animals	Geology – General	Mgmt./ Administration	Social Science – Geography	Watershed Mgt.
y	Exotic Sp. – Plants	Geology – Structural	Microbiology	Social Science – History	Wetlands
Archeology	Fire	Geomorphology	Minerals Management	Social Science – Sociology	Wildlife Management
Botany	Fisheries Management	Geophysics	Oceanography	Social Science – Other	Zoology
Cave (Flora/ Fauna)	Flood Mgmt./ History	Glaciology	Ornithology	Soil Science	
Cave/ Karst	Forestry	Herpetology	Paleontology	Tectonics	Other
Climatology	Fungi	Hydrology (Ground)	Petrology/ Mineralogy	Threat./ Endangrd Animals	
Coastal/ Marine Systems	Geo-Hazard (Chemical)	Hydrology (Surface)	Range Management	Threat./ Endangrd Plants	
Contaminants/ Haz.	Geo-Hazard (Physical)				
Mat.					
Objectives (maximum 4000 characters) The objective of this study has been to determine if semi-volatile organic compounds in the YNP snow pack and snow melt can be attributed to snowmobile traffic. In addition, it was desired to determine whether these compounds accumulate in the snow to levels which pose an environmental hazard and to provide a preliminary estimate of the extent of their persistence in the impacted area. Although EPA has designated polyaromatic hydrocarbons (PAHs) and other semi-volatile organic species as priority pollutants, there have been very few studies of these species in snow pack. During the 1999 Winter season, analysis of the samples was confounded by sampling artifacts and low analytical sensitivity. This seasons work has focused on development of reliable methods for sample collection and analysis of semi-volatile species from mobile sources in snow.					
Findings and Status (maximum 4000 characters) Because of contamination problems observed in all of the 1998-1999 samples, which will be discussed in the results section, the sampling protocols were significantly modified during the 1999-2000 winter season. Samples were collected in 20 quart (18.75 L) stainless steel pots with recessed lids. The containers were washed thoroughly with detergent followed by an acetone rinse to remove any oils that may have adhered to the inner surface of the container. The containers were then rinsed twice with distilled water and sealed until the time of sample collection.					

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wall of the snow pit. Initial samples were used to develop the method. Three final samples were taken approximately 50 meters east of the West Entrance on March 6 at the close of the YNP snowmobile season. The West Entrance has the highest level of snowmobile traffic in the park and so these samples are representative of the total accumulation of semivolatiles in the snow pack during the snowmobile season. One sample was taken right at the edge of the road and included snow that had been removed from the road during grooming of the trail. A second sample was taken 7 meters from the road and the third sample was taken 17 meters from the road. A fourth sample was taken, using the same procedure, from a site 17 meters from the road near the Fawn Pass trailhead in the Gallatin Canyon section of the park. This is a section of the park which receives snowfall similar to the West Entrance, but is impacted by automobile rather than snowmobile traffic. The snowmobile trail nearest this site is the Big Sky trail, which is over 5 miles from the Fawn Pass trailhead and would be expected to exhibit no more than minimal influence at this site.

The samples taken near the West Entrance contained a variety of high molecular weight n-alkanes, n-organic acids, and PAHs, which are most probably attributable to snowmobile emissions. None of these compounds were detected in the snow collected at the Gallatin Canyon site where there was no snowmobile traffic. Table 1 contains a summary of the n-alkanes identified in the snow. N-alkanes are a major constituent of two-stroke engine lubricants. Their concentration in the West Entrance snow samples ranged from 3.67 ppm to 0.19 ppm. The concentrations of all of the n-alkanes dropped rapidly with increasing distance from the road. The combined concentration of the alkanes drops by 39% at 7 meters from the road and by 89% at 17 meters from the road. This pattern also occurs in the concentration of the n-alkyl acids. Table 2 summarizes the data for the n-alkyl acids detected. Exact quantitation of the n-alkyl acids is not available but their normalized concentrations, relative to the amount detected at the road, are presented in Table 2. Their concentration drops by an average of 40% at 7 meters from the road and by 90% at 17 meters from the road. These organic acids are expected partial oxidation products of n-alkanes found in engine lubricants.

Table 3 contains a summary of the concentrations of several EPA priority pollutants detected in the snow samples. Benzene, a component of gasoline, was detected in two of the snow samples collected at the West Entrance, but because EPA method 525.2 is not designed for accurate measurement of volatile compounds the benzene could not be accurately quantified. Its detection in the samples at all is significant since most of the benzene should have been lost during sample preparation.

The PAHs naphthalene, fluorene, and phenanthrene were detected in the samples collected at the West Entrance. Naphthalene was present at a concentration of 25.83 ppb at the edge of the road and its concentration dropped by 80% at 17 meters from the road. Fluorene and phenanthrene were detected at levels below 0.1 ppb and their concentration dropped below detection limit further from the road. Quantitation of these compounds was difficult and may be inaccurate because of interference from the much more concentrated alkanes in the sample and because the concentrations of these compounds were very close to the detection limit. Naphthalene and phenanthrene have been previously identified in two-stroke engine exhaust. Two phthalates were also detected in the samples and their concentrations are shown in Table 3. Their concentrations are not strongly correlated with the other snowmobile-related compounds so they are most likely attributable to another source. Phthalates are common laboratory .

N-alkanes and n-alkyl acids were detected in the multiple ppm range in snow samples taken near the West Entrance at the end of the 1999-2000 winter snowmobile season. The concentrations of these compounds dropped rapidly within a few meters of the road. None of these compounds were detected in the snow collected near the Gallatin Canyon road where there is winter automobile traffic but no snowmobile traffic. The profiles of the compounds and their presence in two-stroke engine lubricants indicates that these pollutants can be confidently attributed to snowmobile traffic. Because of the low efficiency of two-stroke snowmobile engines, these chemically unoxidized lubricant compounds are the predominant semi-volatile organic species found in the snow pack in the heavily trafficked snowmobile areas.

A variety of priority pollutants including benzene, naphthalene, fluorene, and phenanthrene were detected in much lower concentrations and were also strongly associated with the heavily trafficked snowmobile areas. Although the concentration of these compounds is near the detection limit of the method, it is still of serious concern because of their toxicity. Oris et al⁷ have found toxic effects on fish and zooplankton when total PAH

level in the snowpack adjacent to the road at the Yellowstone West Entrance, but direct comparison of these values is not appropriate. In the work by Oris et al the PAHs were emitted directly into the water, which was then taken to the laboratory where it's toxicity to zooplankton and fish was measured. It would be expected that the toxicity of PAHs to organisms in the snowpack might differ significantly from their toxicity in water. In addition, without further study it is impossible to assess the concentration that might be found in water during the snow melt.

Because the concentration of these organic pollutants dropped rapidly within a few meters of the road, the impact on the overall watershed is likely to be minimal but the local impact may still be significant. The snowmobile corridors are typically on roads next to rivers, streams and ponds. In order to assess the ultimate impact on water quality, it will be necessary to trace where these compounds go during the snow melt. The impact of these toxic compounds on aquatic species will be much greater if these pollutants are concentrated in ponds or soil along the roadside during the melt than if they are quickly diluted in rivers or lakes.

In order to fully assess the environmental impact of these snowmobile pollutants we recommend that further studies be conducted to verify that the chemistry observed in these samples is representative of other areas along the snowmobile corridor. Additionally, we recommend that the concentration of the compounds in the snow pack be monitored during the snow melt to determine whether they wash out quickly in the melt or accumulate in the snow pack as it decreases. Analysis of semi-volatile organic compounds in the surface water near the road should be monitored during the snow melt and toxicity studies of the melt water should be evaluated.

Reports Produced (Reference Title, Authors, Name of Publication, Abstract, Volume and Page Numbers, Year Published, Type of Reference, Keywords)

For this study, were one or more specimens collected and removed from the park but not destroyed during analysis? (Y/N) No

If "Yes", where are the specimens currently stored?

Funding provided this reporting year by NPS (enter dollar amount)

Funding provided this reporting year by other sources (enter dollar amount)

List other U.S. Government Agencies supporting this study and funding each provided this reporting year:

Fill out the following ONLY IF the National Park Service supported this project in this reporting year by providing money to a university or college

Full name of college or university

Montana State University

Name of department or program

Dept. of Chemical Engineering

Name of campus, if unique

Bozeman

Annual funding provided by NPS to university or college this reporting year

Table 1
Concentration of N-Alkanes Detected in Yellowstone Snow Samples (in ppm)

Species Found	West Gate at road (ppm)	West Gate 7 meter from road (ppm)	West Gate 17 meter from road (ppm)	Gallatin Canyon 17 meter from road (ppm)
N-Alkanes				
Pentadecane	D	D	D	ND
Hexadecane	1.78	0.58	0.21	ND
Heptadecane	3.43	1.70	0.19	ND
Octadecane	3.42	2.11	0.36	ND
Nonadecane	3.67	2.36	0.45	ND
Eicosane	3.35	2.76	0.46	ND
Heneicosane	D	D	D	ND
Docosane	D	D	D	ND

D -- Compound detected but not quantified

ND -- Compound not detected

Table 2
Concentrations N-Alkyl Acids Detected in Yellowstone Snow Samples
(as percentage of concentration detected at West Entrance Road)

Species Found	West Gate at road (ppm)	West Gate 7 meters from road (ppm)	West Gate 17 meters from road (ppm)	Gallatin Canyon 17 meters from road (ppm)
C-10 Acid	D	D	D	ND
C-12 Acid	100 %	90.1%	19.1%	ND
C-14 Acid	100%	79.2%	11.6%	ND
C-16 Acid	100%	42.4%	5.4%	ND
C-18 Acid	100%	24.8%	3.2%	ND

D -- Compound detected but not quantified

ND -- Compound not detected

Table 3
Concentrations of PAHs and other EPA Priority Compounds
Detected in Yellowstone Snow Samples (in parts per billion)

Species Found	West Gate at road (ppb)	West Gate 7 meters from road (ppb)	West Gate 17 meters from road (ppb)	Gallatin Canyon 17 meters from road (ppb)
Benzene	D	D	ND	ND
Naphthalene	25.83 ppb	24.54 ppb	5.175 ppb	ND
Fluorene	0.062 ppb	0.011 ppb	ND	ND
Phenanthrene	0.183 ppb	ND	ND	ND
Dibutyl Phthalate	0.332 ppb	0.313 ppb	0.122 ppb	ND
Bis(2-ethylhexyl) phthalate	1.93 ppb	2.00 ppb	1.60 ppb	D

D -- Compound detected but not quantified

ND -- Compound not detected